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<p>(21) International Application Number: PCT/US91/02640 (22) International Filing Date: 17 April 1991 (17.04.91)</p> <p>(30) Priority data: 509,856 17 April 1990 (17.04.90) US 613,612 15 November 1990 (15.11.90) US</p> <p>(71) Applicant: LOCTITE LUMINESCENT SYSTEMS INC. [US/US]; Etna Road, Lebanon, NH 03766 (US).</p> <p>(72) Inventor: FARIA, Sixdeniel ; 7057 San Marino Drive, El Paso, TX 79912 (US).</p> <p>(74) Agents: LINEK, Ernest, V. et al.; Dike, Bronstein, Roberts & Cushman, 130 Water Street, Boston, MA 02109 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>																						
<p>(54) Title: ELECTROLUMINESCENT PHOSPHORS WITH LONG LIFE AND METHOD FOR MAKING THE SAME</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Mortaring Time (min)</th> <th>Initial Brightness (Foot-Lamberts) (35)</th> <th>Life (in units of 1000 hours) (36)</th> </tr> </thead> <tbody> <tr><td>0</td><td>5</td><td>2.5</td></tr> <tr><td>5</td><td>25</td><td>3.5</td></tr> <tr><td>10</td><td>22</td><td>4.5</td></tr> <tr><td>20</td><td>20</td><td>5.5</td></tr> <tr><td>30</td><td>18</td><td>6.0</td></tr> <tr><td>35</td><td>15</td><td>6.5</td></tr> </tbody> </table>				Mortaring Time (min)	Initial Brightness (Foot-Lamberts) (35)	Life (in units of 1000 hours) (36)	0	5	2.5	5	25	3.5	10	22	4.5	20	20	5.5	30	18	6.0	35	15	6.5
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<p>(57) Abstract</p> <p>A mixture of predominantly zinc sulfide and minor amounts of a copper activator compound and fluxing agents is first fired at about 1200 °C to form particles of a hexagonal crystalline structure. The first-fired mixture is mortared or otherwise mechanically stressed for variable periods of time beyond its maximum brightness stress period. This material is fired a second time at about 750 °C and cooled to produce the phosphor powder. A number of electroluminescent test lamps (Fig. 1) were made incorporating the various experimental phosphors (30) and each of the different mortaring times. For each phosphor made, the brightness rose, peaked and decreased as mortaring time increased (35), but the life characteristic remained a positive function of mortaring time for a substantially longer time than did the brightness (36). An excellent combination of brightness and life is obtained by mortaring beyond the time required for maximum brightness.</p>																								

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ELECTROLUMINESCENT PHOSPHORS WITH LONG LIFE
AND METHOD FOR MAKING THE SAME

FIELD OF THE INVENTION

This invention relates to electroluminescent phosphors and a method for making such phosphors. In particular, this invention relates to long life phosphors, preferably zinc sulfide based phosphors, obtained by a specially controlled mechanical deformation of an initially fired crystalline zinc sulfide phosphor precursor material. While the phosphors of the present invention may be controlled to emit light in a broad spectrum of colors, the present invention is particularly suited for the manufacture of phosphors emitting in the blue, blue-green, green and yellow-orange portions of the spectrum.

This invention also relates to electroluminescent lamps and a method for making such lamps. In particular, the present invention relates to electroluminescent lamps having unexpectedly long life and retained high brightness.

BACKGROUND OF THE INVENTION

Electroluminescent (EL) phosphors, particularly

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zinc sulfide phosphors, and method for their manufacture are well-known. While such phosphors can be controlled to emit light in a broad spectrum, especially common phosphors emit light in the green and blue portions of the spectrum.

Blue EL phosphors are known for their poor life. The half life (time at which the brightness of the phosphor is one-half the initial brightness) for many blue EL phosphors is in the range of from about 100 to 300 hours when the phosphors are excited at 115 volts and 400 Hz. The half lives are even shorter when these phosphors are used at higher voltages and frequencies.

Green EL phosphors have longer half lives than blue EL phosphors, typically in the range of about 10-1000 hours at 115 volts, 400 Hz; but they also exhibit shortened half life when subjected to higher voltages and/or frequencies. The foregoing data is based upon typical EL lamp constructions wherein the blue phosphor typically emits light in the 15 ft-L range and the green EL phosphor typically emits in the 25 ft-L range.

Blue EL phosphors are normally prepared by firing zinc sulfide, a copper activator, and one or more halide fluxes at high temperatures. Phosphors such as ZnS:Cu:X (X=Cl or Br) containing more than about 0.05 weight % Cu are typically blue-green rather than blue. It is known that as the copper content increases, there is a gradual shift in the light emitted from blue to green. Similarly, a yellow-orange shift in emitted light can be achieved by adding manganese to conventional ZnS:Cu phosphor materials. West German Patent No. 3,011,815 (Fischer) claims a long life blue

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phosphor consisting of zinc-cadmium sulfide containing magnesium sulfide "to give a blue shift," however no absolute values for "long life" are provided in the patent to verify this claim.

For many years, various techniques have been proposed for improving the brightness and half life of zinc sulfide phosphors activated with copper. Often, these techniques have involved the addition of one or more coactivators such as halide (e.g. Cl, Br, I) or trivalent ion (aluminum, gallium, indium, etc.) compounds or complexes. See, for example, U.S. Patent Nos. 3,082,344 (Thornton), 3,152,995 (Strock) and Peters, et al. (J. Appl. Phys., 34:2210-2215, (1963)) which describe various method for manufacturing such phosphors with the objective of improving their brightness.

Zinc sulfide electroluminescent phosphors of the prior art have typically been prepared via the steps of: (a) preparing a mixture of predominantly zinc sulfide, about one weight percent of an electroluminescent activator (e.g., a copper compound such as CuSO₄) and a few weight percent of a halide coactivator fluxing compound; (b) firing this mixture, e.g., at from about 1000°C to 1300°C; (c) allowing this first-fired material to return to room temperature and washing with water; (d) mechanically stressing the first-fired material (e.g., by milling); (e) firing (baking) the deformed powder at an elevated temperature, e.g., from about 600°C to 950°C; and (f) bringing this second-fired powder material back to room temperature (e.g., either by removing it from the oven and allowing it to cool slowly, or by cooling

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slowly and then quenching).

In the process described above, the first firing causes a transformation of the initially predominantly cubic structure of the phosphor precursor material to a predominantly hexagonal conformation. Upon the subsequent cooling, there is some reversion of the hexagonal conformation to the cubic conformation; however, such reversion is minimal. The mechanical stressing step further reverts more phosphor to the cubic conformation and introduces "faults" within the phosphor particle. The second firing and cooling cycle results in the further transformation of the phosphor particles back to a predominantly cubic structure.

It is generally accepted in the phosphor art that the reversion of the phosphor back to a predominantly cubic structure or conformation is necessary to attain brightness and life. In following therewith, it is recognized that the parameters of a mechanical stressing step are critical for promoting or attaining a sufficient level of reversion to the cubic structure to obtain a commercially useful phosphor. Such deformation is typically accomplished by milling or mulling the first-fired material for a standard period of time, i.e., that which by prior experiments and/or experience has afforded the manufacturer with maximum phosphor brightness.

While the art teaches that various stressing steps may be employed for fracturing the first-fired zinc sulfide crystals, none of these processes have resulted in zinc sulfide phosphors having both the high initial brightness and the long half life with the retained

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high brightness of the phosphors of the present invention.

SUMMARY OF THE INVENTION

As described above, the present invention relates to electroluminescent phosphors and to a method for making such phosphors. In particular, the present invention relates to phosphors having long life obtained by a specially controlled mechanical deformation of an initially fired crystalline zinc sulfide phosphor precursor material.

It is known in the phosphor art that duration is a key parameter of the mechanical stressing step in order to attain maximum brightness. Generally, it has been shown that the initial brightness of a phosphor product increases during the early periods of mechanical stressing to a maximum brightness level and thereafter decreases with continued stressing. See Peters, et al., supra. It has now been unexpectedly discovered that the characteristic time to half brightness of the electroluminescent phosphor product (i.e., the half life) is a positive function of mechanical stressing time, not only up to the time that brightness peaks, but beyond that time as well. This phenomenon has been found to exist for all variations of parameters employed in the processes used for making electroluminescent phosphors thus far explored.

Furthermore, it has been discovered that the rate at which the phosphor brightness tends to decrease with continued stressing after peak brightness has been

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achieved is substantially slower than the rate at which brightness increases with stressing before peak brightness is reached. Thus, the present invention is based upon the discovery that extreme mechanical stressing of a first-fired phosphor precursor material, i.e., stressing for a period of time beyond that at which peak brightness is normally realized, yields an electroluminescent phosphor product having unexpectedly superior properties in terms of both brightness and useful life (i.e., improved half life with little sacrifice in brightness).

The critical factor for obtaining the improved properties in electroluminescent phosphors in accordance with the present invention is the performance of the mechanical stressing of the first-fired phosphor precursor material. As noted, it is critical that this mechanical stressing be performed for a period of time which exceeds that at which maximum brightness is attained for the given phosphor material. The specific parameters chosen for the mechanical stressing step will depend upon the starting materials, the type of mechanical stressing imparted upon the phosphor, the efficiency of the apparatus or methodology employed in stressing the phosphor precursor, as well as the brightness and life characteristics desired of the final phosphor product. With respect to the starting materials, it is found that the addition of high levels of the copper activator, besides resulting in a more green phosphor, results in phosphors having longer life and higher brightness as compared to similar phosphors employing less copper activator. Furthermore, it is also found that a small quantity of zinc selenide added to the

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starting material will also contribute in a beneficial way to the quality of the EL phosphor so produced, particularly with respect to the production of high brightness and excellent long life green phosphors.

The process of the present invention thus comprises the following steps:

- (a) preparing a mixture of a predominant amount of zinc sulfide and a minor amount of an activator compound, preferably a copper-containing activator compound;
- (b) firing the mixture (first fire) at a temperature sufficient to form particles having a predominantly (>50%) hexagonal crystalline structure;
- (c) mechanically stressing the first-fired mixture, e.g., by mortaring, mulling or milling, for period of time exceeding that at which maximum brightness would be achieved;
- (d) firing the mechanically stressed material for a second time (second fire), to complete the reversion of the crystalline structure to a predominantly cubic conformation; and
- (e) subsequently cooling the twice-fired material to yield the desired high brightness, long half life electroluminescent phosphor products.

The present invention is generally applicable to all electroluminescent phosphors, regardless of color emittance, but is particularly applicable to phosphor materials emitting in the blue, green and yellow-orange portions of the spectrum. Ultimate coloration of the finished phosphor is dependent, at least in part, upon the starting materials employed. Variations in coloration may be effected by varying the constituents

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and relative amounts of the constituents in said starting materials, as is well-known by those of ordinary skill in the phosphor arts. For example, the brightness and color may be controlled by shifting the copper and/or zinc selenide content.

In any event, many improvements and attributes are realized from the phosphors produced in accordance with the practice of the present invention as compared with typical, comparable phosphors. For example, phosphors made in accordance with the practice of the present invention which emit in the green portion of the spectrum have half lives in excess of 2000 hours to over 10,000 hours, as compared with its standard counterparts which typically have half lives of only about 1000 hours. Similarly, blue electroluminescent phosphors produced in accordance with the practice of the present invention typically have half lives 3 to 5 times longer than those of traditional blue phosphors.

In addition to the improved phosphors and improved process for making phosphor as described above, the present invention also relates to electroluminescent lamp elements having superior life and brightness characteristics. The improved electroluminescent lamps of the present invention result from the incorporation of the phosphors produced in accordance with the practice of the present invention into typical electroluminescent lamps. The construction and method of manufacture of these EL lamps is well-known and well-described in the patent literature.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a side sectional view of the electroluminescent lamp used for testing phosphors of this invention.

Figures 2 through 6 are plotted curves, corresponding to each of a number of different phosphor compositions which were incorporated into test electroluminescent lamps, showing how the characteristic brightness and life of each phosphor product changes as a function of the duration of mechanical stressing during processing.

Figure 7 shows the brightness and life characteristics versus stressing time for a phosphor composition wherein the stressing is brought about by mulling.

Figure 8 shows the life characteristics of a zinc sulfide:copper phosphor stressed for 20 minutes by mortaring, wherein the retained Cu content was sequentially elevated from 0.054% through 0.091%, and, for comparative purposes, the life characteristics of a comparable commercial green EL phosphor. The commercial phosphor has a retained Cu content of 0.08% and showed shorter life than the 0.054% Cu content phosphor from the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention is generally applicable to any electroluminescent phosphor precursor

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material or composition. Such compositions are well-known and readily recognizable by those of ordinary skill in the art.

Typical phosphor precursor materials generally comprise zinc sulfide, alone or in combination with zinc selenide, an activator therefore, and one or more coactivators. In preferred phosphor precursor compositions, a combination of zinc sulfide and zinc selenide is employed. This zinc sulfoseleide mixture generally comprises at least 80%, preferably 90%, and most preferably, at least 96% by weight zinc sulfide, with the remainder comprising the zinc selenide.

Activator compounds which may be used in the phosphor precursor compositions of the instant invention include, but are not limited to, copper, silver, gold, phosphorus, arsenic, vanadium, antimony, lead, tin, manganese, iron, sodium, lithium, gallium, tellurium, scandium, indium, and rare earth compounds. The preferred activator comprises a copper compound, alone or in combination with one or more of the other aforementioned activator compounds. Preferred copper compounds include copper sulfate, copper nitrate, copper chloride, copper bromide, copper acetate, copper fluoride, copper iodide and copper carbonate; with copper sulfate being most preferred. Generally, the activator will be present in an amount of less than 4%, preferably less than or equal to about 1% by weight, based upon the aforementioned zinc sulfide or zinc sulfoseleide materials.

Coactivators that may be employed in the practice of the present invention include compounds or complexes

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of halide (Cl, Br, I) and trivalent ions (Al, Ga, In, etc.). Preferred coactivators include complexes based on halides, most preferably halide fluxes. Suitable coactivators are well-known to those of ordinary skill in the art. Exemplary of suitable coactivators there may be given barium bromide, magnesium bromide, sodium bromide, magnesium chloride, ammonium bromide, sodium chloride, barium chloride, magnesium iodide, ammonium iodide, barium iodide, sodium iodide, and the like. Generally, the coactivator is present in its hydrated form, e.g., magnesium chloride (hydrated) ($MgCl_2 \cdot 6H_2O$). The coactivator component may comprise one or more coactivators and is generally employed in an amount of 20% by weight or less, preferably 10% by weight or less, and, most preferably, about 8% by weight or less, based upon the weight of the zinc sulfide or zinc sulfoselenide material.

As noted, additional constituents may be added or incorporated into the phosphor precursor mixture or composition as desired. Such additional constituents include zinc sulfate, zinc oxide, sulfur and the like, and will be readily known to those skilled in the art.

While the exact reasons for the improved results obtained by Applicant's process are not fully understood, the results are quite clear. The present invention provides a zinc sulfide phosphor which, when emitting in the green portion of the spectrum, has a half life in excess of 2000 hours and, when emitting in the blue portion of the spectrum, has a half life in excess of 1000 hours, both of which represent dramatic improvements over existing comparable emitting phosphors.

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Briefly, the present invention starts with the aforedescribed phosphor precursor materials or compositions. Preferably, said mixture comprises a mixture of cubic or predominantly cubic zinc sulfide and a copper activator, e.g., copper sulfate, and at least one coactivator such as a halide flux (e.g., a chloride or bromide flux). This precursor composition is fired at a temperature and for a period of time sufficient to convert the cubic conformation of the zinc sulfide to a predominantly (> 50%) hexagonal conformation. Appropriate temperatures and time for this firing will be readily apparent to those of ordinary skill in the art. Typically, the first firing will be conducted at a temperature of at least about 1000°C, preferably of at least 1100°C, most preferably of at least about 1200°C. However, the maximum firing temperature will generally not exceed 1400°C. The period of time for which the phosphor precursor material is subject to said firing will depend upon the precursor materials and the temperature of the firing itself. Generally, the first firing will be for a period of time of from about 1 hours to 6 hours, preferably from about 2 hours to about 4 hours. It should be noted that all reference within this specification, including the examples, to firing time, is to be understood as the time of the actual firing of the phosphor precursor or phosphor material from when the temperature of the material achieves the firing temperature until the firing is completed. Thus, the actual residence time in the furnace will be somewhat longer than the firing times so as to allow the phosphor materials to attain the desired firing temperature.

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After firing, the first-fired materials are allowed to cool to allow the same to be further processed. During said cooling cycle, which may be an ambient cooling or a forced cooling, some of the crystalline zinc sulfide will revert from the hexagonal conformation to the cubic conformation.

The first-fired materials are then milled or mortared in a mortar-grinder, for example in a Model RMO mortar-grinder made by Retsch GmbH of West Germany, for a period of time in excess of that at which maximum brightness is achieved (T_b). T_b is easily determined through simple and undue experimentation for any given phosphor composition and/or is well-known in the art for standard phosphor compositions. The purpose of the extended milling process is to produce a highly fractured zinc sulfide crystal.

While it is known that milling will induce faults or fractures into the crystalline structure of the zinc sulfide particles, because phosphors have typically been rated on brightness, it was believed to be detrimental to mill for extended periods of time and thus induce a degree of faulting or fracturing beyond that at which maximum brightness was attained. Unexpectedly, however, it has now been found that continued milling and, thus, the inducement of higher levels or degrees of faulting or fracturing in the zinc sulfide crystals results in phosphors having far superior lives with only minimal loss in brightness.

In addition to producing a more highly fractured or faulted zinc sulfide crystal, the milling also causes the conversion of some of the zinc sulfide crystals

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from the hexagonal conformation to the cubic conformation and, perhaps more importantly, appears to facilitate the subsequent and more extensive crystalline phase transition from hexagonal to cubic conformation caused by the second firing step. It has also been found that continued milling may lead to a more uniform and smaller particle size, which from the standpoint of phosphors useful in the manufacture of electroluminescent lamps may be desirable, but is not otherwise believed to be critical.

The specific length of time for which the first-fired materials are mechanically stressed is dependent upon the materials themselves, the desired final properties and characteristics, and the mechanical stressing technique or methodology employed. Exemplary of the method by which stressing can be accomplished include mortaring, mix-mulling, ball milling, fluid-energy milling, jet pulverization, grinding, vibratory milling, centrifugal milling, hydrostatic pressure, uniaxial or biaxial pressure and the like. Furthermore, this invention is also intended to encompass mechanical stressing by means other than directly applied external forces as exemplified above. Although not yet attempted, such other methods include subjecting the material to thermal shocks or other shocks that would most certainly entail a mechanical stressing of the individual particles of the in-process phosphor.

Concurrent with or subsequent to the mechanical stressing steps, additional activators, coactivators, or other co-constituents may be added to the in-process phosphor mixture. Such additives or dopants, as they

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are sometimes referred, are as previously defined. In general, it is preferred to add additional activators, preferably copper activators, alone or in combination with other co-constituents. A preferred combination of dopants to be used at this point include copper sulfate and zinc sulfate. Generally, the amount of activator added to the in-process phosphor will be from about 0.5% to about 5%, preferably from about 1% to about 3%, by weight based upon the total weight of the in-process phosphor. While lower amounts may be employed, such amounts are less likely to provide as much improvement in brightness and life in the final composition. However, said compositions will still have properties superior to conventional phosphors. Similarly, while higher amounts of the activator may be employed, it is believed that amounts of the activator may be employed, it is believed that amounts in excess of the 5% by weight are beyond the saturation point for the composition and, thus, generally do not provide any further improvement in brightness and/or life.

With respect to the co-constituent, the co-constituent is preferably employed in an amount of from about 1% to about 20%, preferably from about 1% to about 16%, by weight based upon the total weight of the in-process phosphor. As noted previously, the preferred combination of dopants added during or following the first firing comprises copper sulfate and zinc sulfate.

The mixture is then refired at a temperature lower than the initial firing, generally less than about 1050°C, preferably less than about 900°C. The most preferred second firing temperatures range from about

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750°C to about 800°C. The length of time for which the second firing is conducted will generally depend upon the firing temperature, the materials themselves and the desired characteristics and properties of the final phosphor materials. Generally, the time of firing is that time which is sufficient to complete reversion of the conformation of the crystalline structure from a hexagonal conformation to a predominantly cubic conformation. This time is generally on the order of one-half hour to 3 hours or more. Preferred firing times for the second firing are on the order of one-half hour to 2 hours, more specifically 1 hour to about 2 hours.

Following the second firing, the phosphor materials are allowed to cool, either atmospherically or by induced cooling or quenching. Thereafter, the phosphor particles are treated or washed to remove excess activator, e.g., copper compounds, from the surface of the zinc sulfide crystals. Such washings may be accomplished by any methods known in the art. Exemplary of such methods include a multi-step washing employing, in sequence, hydrochloric acid (4N), water and a 4% sodium cyanide solution. Following washing, the phosphor materials are dried.

After drying, the phosphor is preferably sieved through a 325 mesh screen so as to remove all excessively large phosphor particles. Although the unsieved phosphors do provide the attributes of long life with high brightness, they are less desirable for use in the manufacture of electroluminescent lamps which have preferred particle size tolerances for insuring a good phosphor layer in its construction.

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In addition to the foregoing steps, other steps or processes may be conducted at various times in the process as described above. For example, following the initial firing, it may be desirable to wash the in-process phosphor materials with water so as to remove the excess coactivators, including any ions thereof that may have formed, especially any excess halide ions. Such washing may be accomplished with repeated treatments with hot, deionized water until the conductivity of the wash water is below certain levels, preferably less than about 50 micromho cm⁻¹. Additionally, it may be desirable to sieve the first-fired materials to remove any excessively large particles. Generally, at this stage, it is preferred to employ a 100 mesh screen for sieving purposes.

Although not intending to be bound by theory, it is believed that in the practice of the instant process the initial high temperature firing, combined with the excessively long period of mechanical stressing, leads to phosphor particles having a higher degree of faults or fractures in the crystalline structure as well as to phosphor compositions having a higher level or percentage of particles having the cubic as opposed to the hexagonal conformation. It is believed that the increased number of fractures or faults in the zinc sulfide particle provides additional sites for activator, copper compound, deposition during the second firing.

The doping of the first-fired material with additional copper activator tends to increase the likelihood of saturation of the numerous faults or fractures in the crystalline structures. Obviously,

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with very low levels of copper activator in the in-process mixture, the opportunity or likelihood of the copper compound to infiltrate the fracture or fault is less likely than in instances where high levels of copper activator are employed. In general, the amount of initial copper and added copper is maintained sufficiently high during the two firing steps such that the total retained copper content of the final product after washing is at least 0.02%, preferably at least 0.06%, by weight. In general, the total retained copper content will preferably be in the range of 0.04% to about 0.25%, most preferably about 0.06% to about 0.2%, by weight of the phosphor mixture. Compositions within the foregoing limitation and manufactured in accordance with practice of the present invention generally provide phosphors having high initial brightness and a long half life.

To determine the effect of mortaring time on phosphor performance, several series of electroluminescent phosphors were manufactured and electroluminescent test lamps produced with said phosphors. Each series differs from one another by some variation in the method for making electroluminescent phosphor and/or the compositional makeup of the phosphor precursor materials. Within each series, the phosphor and its method of manufacturing were held constant while the phosphor mortaring time was varied. Each phosphor sample was then incorporated into five electroluminescent lamps and the lamps tested.

The EL test lamps (illustrated in Figure 1) were prepared as follows. A paste was formed by dispersing

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the electroluminescent phosphor powder in a dielectric resin. A layer of the phosphor powder paste 30 and a layer of a barium titanate paste 34 are sandwiched between an opaque metallic foil (aluminum) servicing as a rear electrode 20 and a transparent front electrode (indium tin oxide) 22. A layer 24 of a desiccant is formed over the front transparent electrode 22. A pair of lead wires 26 and 28 are attached, respectively, to the front and rear electrodes 22 and 20. A polymeric protective film 32 encapsulates this assembly, but with the lead wires 26 and 28 extending away therefrom, to provide physical support and a moisture barrier. The phosphor layer 30 has a thickness of 0.04 millimeters. The barium titanate layer 34 is 0.015 millimeters thick.

A more detailed description of the construction of an electroluminescent lamp is provided in U.S. Patent No. 4,104,555 (Fleming), the disclosure of which is hereby incorporated herein by reference.

The general method for making the phosphor as described above will be referred to hereinafter as the reference method.

In the following examples, the brightness of each test lamp was measured with excitation at 115 volts and 400 Hz. The brightness and life date points for each phosphor produced were determined by averaging the measured brightness and life for each of the five test lamps per group. By convention, the half life of an electroluminescent phosphor (or lamp containing the same) is defined as the time required for the initial brightness (B_0) to decrease to one-half of its

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initial value. Since this time may be several thousand hours, an accelerated life test is a near necessity. One such test was devised by British Aerospace and consists of operating lamps at elevated temperature and frequency. This method is described in R.H. Marion et al. "Analysis of the Lifetime and Powder Electroluminescent Phosphors" in Electroluminescence, Shionoya, S. and Kobayashi, H., Ed., Springer-Verlag, P. 332, 1989.

The accompanying figures represent the brightness and life data realized from evaluations of various phosphors made in accordance with the practice of the present invention as set forth in the following examples. Figures 2 through 6 are graphic representations of the life and brightness data versus mortaring time for compositions made in accordance with the practice of the present invention. Figure 7 illustrates the effect on brightness and life of mulling rather than mortaring. Figure 8 represents data demonstrating the effect on life of various levels of retained copper in the phosphor. Figures 2, 3 and 6 are based on actual life test data. All other figures represent life data which are based on accelerated life test results. Figure 2 sets forth the actual data points arrived at, whereas Figures 3 through 7 present the brightness and life data in a normalized fashion, i.e., the data points representing the greatest level of brightness and life, as measured, are each set to a value of 1.0.

The following examples are intended to aid in the understanding of the present invention, but are not to be construed as limitations thereof. Unless otherwise

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indicated, all amounts with respect to the various constituents of the phosphor precursor materials and the in-process additives are in parts by weight. All temperatures are expressed in degrees Celsius.

EXAMPLE 1

A series of phosphor compositions emitting in the green portion of the visible light spectrum were made according to the following procedure:

98 parts zinc sulfide, 2 parts zinc selenide, 0.3 parts copper sulfate (anhydrous), 3 parts barium bromide (hydrated), 3 parts magnesium bromide (hydrated) and 2 parts sodium bromide were dry blended together in a V-blender for at least one-half hour. The blended materials were then placed in a quartz crucible, covered and fired at 1200°C for 3 hours. After 3 hours firing, the crucible was brought out of the furnace and cooled rapidly with cold air blowing on the bottom of the crucible. Once the phosphor was cooled, it was washed free of ions, especially bromide ions, with hot deionized water at least six times, or until the conductivity of the wash water was less than 50 micromho cm^{-1} . The phosphor was then filtered, dried and sieved through a 100 mesh screen. This step of the process yields a material that is referred to as the first-fired material.

Individual 200 gram aliquots of the first-fired material were then mortared for various lengths of time to demonstrate the effect thereof.

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In this example, mortaring times of 0, 5, 10, 20, 30 and 40 minutes were employed.

Each mortared sample was then doped with 5 grams of copper sulfate ($CuSO_4$) and 32 grams of zinc sulfate ($ZnSO_4$), blended and fired at $800^{\circ}C$ for 1 hour in a covered quartz crucible. Following this second firing, the phosphor was then cooled and sequentially washed with hydrochloric acid (4N), water, and finally a 4% NaCN solution to remove any excess copper found on the surface of the phosphor particles. The phosphor was then dried, sieved through a 400 mesh screen and processed into electroluminescent lamps.

The data representing the brightness levels and half lives attained for the various samples made in accordance with this example are depicted in Figure 2 above. As shown, brightness (curve 35) peaked at a mortaring time of about 5 minutes, whereas the half life (curve 36) continues to increase even up to 30 minutes. Furthermore, although brightness diminishes with continued mortaring beyond the time at which peak brightness is attained, its rate of diminution is much slower as compared to its rate of enhancement in the early stages of milling. Based on this data, it is clearly advantageous to mortar the phosphor beyond the 5 minutes at which peak brightness is obtained, thereby obtaining a significant increase in life at the expense of a minimal loss in brightness. These same plots are depicted in a normalized fashion in Figure 3 as per curves 41 and 42, respectively.

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EXAMPLE 2

A second phosphor composition was made in accordance with the procedure of Example 1 with the exception that the second firing was at 750°C instead of 800°C. This phosphor composition was slightly different from that set forth in Example 1 in that zinc selenide was eliminated from the formulation and that magnesium chloride (hydrated) was substituted on a weight for weight basis for the magnesium bromide of Example 1. The brightness and life data for this sample of phosphor is depicted in a normalized fashion in curves 45 and 46, respectively, of Figure 3.

EXAMPLE 3

A phosphor composition was made in accordance with the procedure of Example 1 with the exception that the amount of copper sulfate starting material was increased from 0.30 parts by weight to 0.40 parts by weight. Brightness and life data, as a function of mortaring time, for this phosphor composition is presented in Figure 4 by curves 51 and 52, respectively.

EXAMPLE 4

A phosphor composition emitting in the blue portion of the spectrum was made in accordance with the procedure of Example 1 except that the level of copper sulfate was reduced from 0.30 parts by weight to 0.15 parts by weight, 1 part by weight of ammonium bromide

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was substituted for the 3 fluxes (barium bromide (hydrated), magnesium bromide (hydrated) and sodium bromide)), and 1 part by weight of sulfur was added as a co-constituent. The brightness and life data for the phosphor so made is depicted in Figure 4 by curves 55 and 56, respectively.

EXAMPLE 5

An additional series of phosphors was made in accordance with the procedure of Example 1 except that the starting materials were blended through a wet mixing effected by the addition of water, which was subsequently removed by heating and drying, and the second firing was conducted at a temperature of 750°C. Additionally, the composition of Example 1 was modified in that the magnesium chloride (hydrated) was substituted on a weight for weight basis for the magnesium bromide. The data points determined for the brightness and life of the phosphor so produced are depicted by curves 61 and 62, respectively, in Figure 5.

EXAMPLE 6

A series of phosphor compositions were manufactured in accordance with the general procedure of Example 1 with the exception that the firing time was varied as set forth below and that a magnesium chloride (hydrated) flux was substituted for the magnesium bromide (hydrated) flux on a weight for weight basis. The first series of phosphors as represented by curves

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71 and 72 (Figure 6), for brightness and life, respectively, were fired for 2 hours in both the first and second firings. On the other hand, curves 75 and 76 correspond to the brightness and life behavior, respectively, of similar series of phosphors with the exception that the first firing was conducted for a period of 2 hours and the second firing for a period of 4 hours. Once again, as shown in Figure 6, the advantages of mortaring beyond the time at which brightness becomes greatest is clearly evident for all of these changes in the method of making the phosphor.

EXAMPLE 7

A series of phosphor compositions as described in Example 1 were prepared in accordance with the method of Example 1 with the exception that the starting materials, following the first firing, were mulled, rather than mortared, and the second firing was conducted at 750°C. The mulling machine employed was a Simpson Mix-Muller, Model LF, Style UD, made by the National Engineering Company of Chicago, Illinois. This device consists of two heavy crusher wheels mounted at the ends of a horizontal axle that rotates in a horizontal plane about the axle center. Sweepers direct the material being mulled under the wheels.

As shown in Figure 7, the phosphors produced in accordance with the above teaching manifested a maximum brightness after 30 minutes of mulling (curve 81). Continued mulling of the phosphor composition beyond the 30 minute peak period resulted in the development of phosphors having a longer life performance with a

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minor loss in brightness (curve 82). This example demonstrates the fact that alternative methods for mechanically stressing the phosphors may be employed in the practice of the present invention. It is recognized that certain mechanical stressing methodologies may require longer periods of stressing in order to achieve the same result. Nevertheless, the practice of the present invention still provides improved phosphor compositions and, subsequently, electroluminescent lamps having enhanced brightness and longevity.

EXAMPLE 8

A series of phosphor compositions was prepared in accordance with the methodology of Example 1 and of the formulation of Example 1 with the exception that the amount of copper added initially was varied so as to provide phosphor compositions having a formulated initial copper content of 0.06%, 0.08%, 0.10% and 0.12% by weight, respectively. The actual lamp brightness and half life data, as function of copper content and mortaring time, is depicted in Table I.

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TABLE I

Relationship of Brightness and Life
to Initial Copper Content and Mortaring Time

<u>% Cu</u>	<u>Mortaring Time (Min.)</u>	<u>Initial Brightness (Ft-L)</u>	<u>Half Life (Hours)</u>
0.06	0	18.9	150
	20	23.2	1900
0.08	0	9.6	200
	20	20.1	4900
0.10	0	9.4	250
	20	24.6	6150
0.12	0	9.5	500
	5	27.5	3200
	10	25.3	5300
	20	22.5	5650
	30	19.3	7700
	40	17.5	7600

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The mortared samples always showed higher initial brightness and better half life than the unmortared samples. The half life also improved with increasing copper content. The 30 minute mortared sample, for the 0.12% Cu, showed a slight decrease in brightness, but continued to show very good half life.

The relationship of brightness and life to copper content is shown in Table II and depicted in Figure 8. Also shown in Figure 8 is the plot of a typical commercial green phosphor which has a retained copper content of 0.08%. After 600 hours operation, the brightness of the EL lamp was only 66% of its initial brightness level.

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TABLE II

Percent Initial Brightness as a Function
of Operating Time

Wt. % Cu	Initial Brightness	Operating Time (Hours)					
		1 Ft-L	16	72	238	406	593
0.06	22.7	101.98	104.9	100.9	88.9	81.7	76.4
0.08	19.9	101.0	100.5	98.8	83.5	90.5	88.0
0.10	23.5	101.2	102.3	100.9	96.0	92.5	90.5
0.12	22.8	100.9	103.1	102.1	96.4	93.3	91.9
							87.2
							87.9

Wt. % Cu	Operating Time (Hours)					
	899	1121	1244	1410	1582	1768
0.06	64.7	61.5	59.6	56.4	53.8	51.5
0.08	80.0	79.9	78.1	75.4	73.6	71.1
0.10	83.7	83.4	81.2	79.7	76.5	76.1
0.12	82.5	82.8	80.5	78.2	77.9	75.2
						73.3
						73.3
						71.9
						51.7

Wt. % Cu	Operating Time (Hours)					
	1937	2082	5180			
0.06						
0.08						
0.10						
0.12						

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The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements of this invention and still be within the scope and spirit of this invention as set forth in the following claims.

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WHAT IS CLAIMED IS:

1. A method for making an electroluminescent phosphor having long life, said method comprising:
 - (a) preparing a mixture of phosphor precursor materials comprising predominantly zinc sulfide and minor amount of a copper activator compound;
 - (b) first firing said mixture to form particles of a predominantly hexagonal crystalline structure;
 - (c) mechanically stressing said first-fired material to produce a crystalline powder, some portion of which is, by said stressing, converted to a cubic structure, said mechanical stressing being continued for a period of time beyond that at which maximum brightness of said finished phosphor would have been realized;
 - (d) subsequently firing said stressed crystalline powder to revert the structure thereof to a predominantly cubic structure; and
 - (e) cooling said subsequently fired powder.
2. The method of claim 1 wherein said stressing time amounts to at least 1.25 times that at which said maximum brightness of said finished phosphor would have been realized.
3. The method of claim 1 wherein additional copper activator, alone or in combination with coactivator or other additive, is added to the mixture during or subsequent to the mechanical stressing step.

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4. The method of claim 3 wherein an additive is employed and the additive is zinc sulfate.

5. The method of claim 1 wherein said first firing is conducted at a temperature of at least 1100°C and said second firing is conducted at a temperature of 900°C or less.

6. The method of claim 1 wherein said first firing is conducted at about 1200°C or more and said second firing is conducted at about 800°C or less.

7. The method of claim 1 wherein the amount of copper activator compound is about 1% by weight or less based upon the weight of the zinc sulfide.

8. The method of claim 1 wherein the phosphor precursor materials further comprise a coactivator.

9. The method of claim 8 wherein the coactivator is a halide flux.

10. The method of claim 8 further including the step of washing the first-fired material so as to remove any excess coactivator for coactivator ions.

11. The method of claim 1 wherein the phosphor precursor material further comprises zinc selenide.

12. A powdered electroluminescent phosphor made in accordance with the method of claim 1.

13. A powdered electroluminescent phosphor made in accordance with the method of claim 8.

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14. A method for making an electroluminescent lamp, said method comprising:
- (a) preparing a mixture of phosphor precursor materials comprising predominantly zinc sulfide and a minor amount of a copper activator compound;
 - (b) first firing said mixture to form particles of a predominantly hexagonal crystalline structure;
 - (c) mechanically stressing said first-fired material to produce a crystalline powder, some portion of which is, by said stressing, converted to a cubic structure, said mechanical stressing being continued for a period of time beyond that at which maximum brightness of said finished phosphor would have been realized;
 - (d) subsequently firing said stressed crystalline powder to revert the structure thereof to a predominantly cubic structure;
 - (e) cooling said subsequently fired crystalline powder;
 - (f) forming a stack with layer of said second-fired crystalline powder dispersed in a dielectric resin sandwiched between a rear electrode and a light transparent front electrode; and
 - (g) attaching a pair of conductive leads respectively to said rear and front electrodes.

15. The method of claim 14 wherein said mechanical stressing time amount to at least 1.25 times that at

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which said maximum brightness of said finished phosphor would have been realized.

16. The method of claim 14 wherein additional copper activator, alone or in combination with a coactivator or another additive, is added to the mixture during or subsequent to the mechanical stressing step.

17. The method of claim 16 wherein an additive is employed and the additive is zinc sulfate.

18. The method of claim 14 wherein said first firing is conducted at a temperature of at least 1100°C and said second firing is conducted at a temperature of 900°C or less.

19. The method of claim 14 wherein said first firing is conducted at a temperature of about 1200°C or more and said second firing is conducted at a temperature of about 800°C or less.

20. The method of claim 14 wherein the amount of copper activator compound is about 1% by weight or less based upon the weight of the zinc sulfide.

21. The method of claim 14 wherein the phosphor precursor materials further comprise a coactivator.

22. An electroluminescent lamp comprising:

- (a) a rear electrode;
- (b) a light transparent front electrode;
- (c) an electroluminescent phosphor dispersed in a

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layer of a dielectric resin, said phosphor comprising a copper doped zinc sulfide which has been prepared in accordance with the method of claim 1, said phosphor containing dielectric resin layer being sandwiched between said rear electrode and said front electrode; and

- (d) a pair of conductive leads attached respectively to said rear and front electrodes.

23. The electroluminescent lamp of claim 22 wherein said copper doped electroluminescent phosphor has been mechanically stressed for a period of time of at least 1.25 times that at which said maximum brightness of said finished phosphor would have been realized.

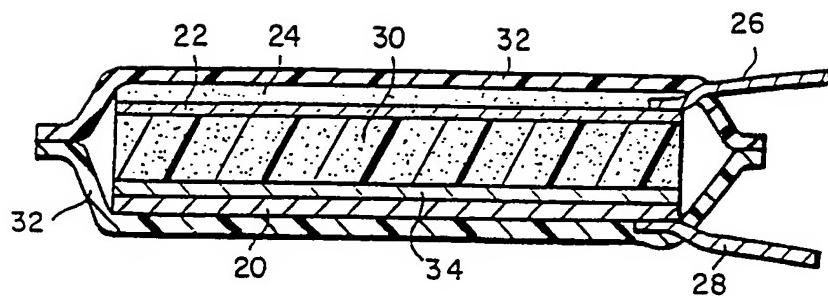


FIG. 1

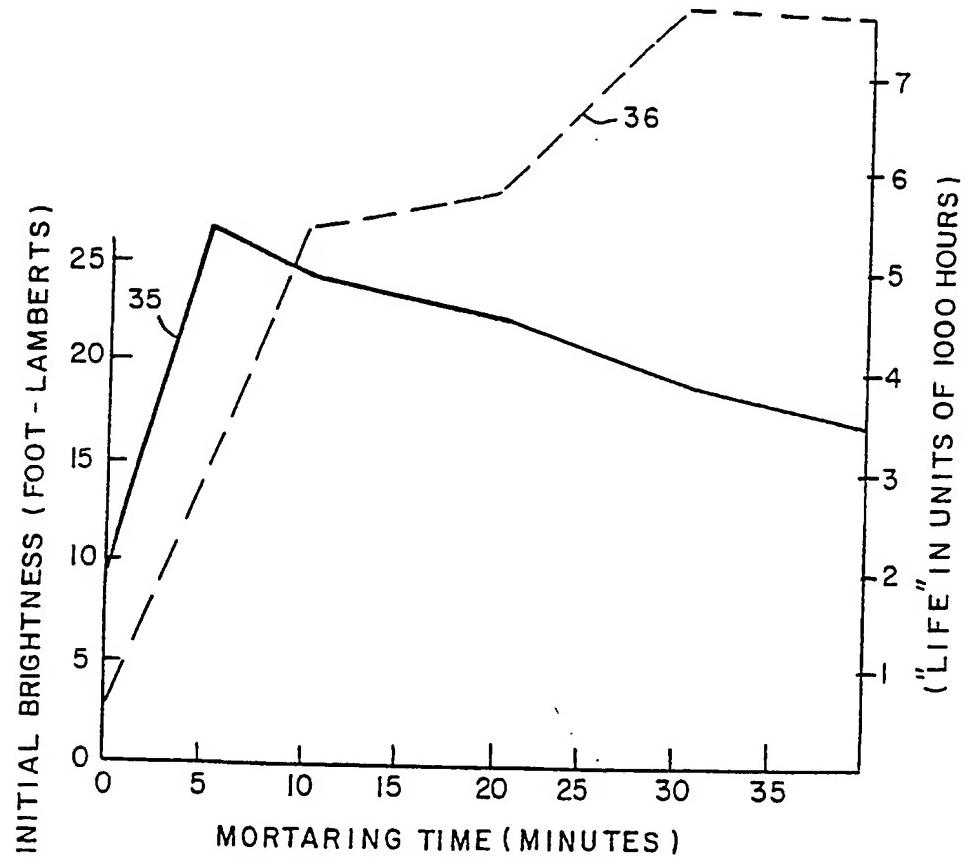


FIG. 2

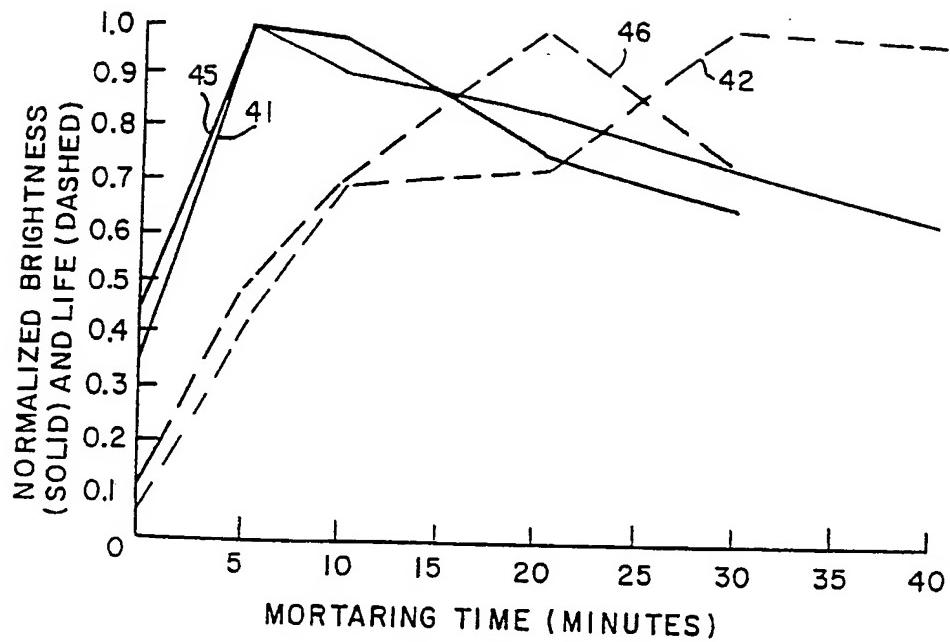


FIG. 3

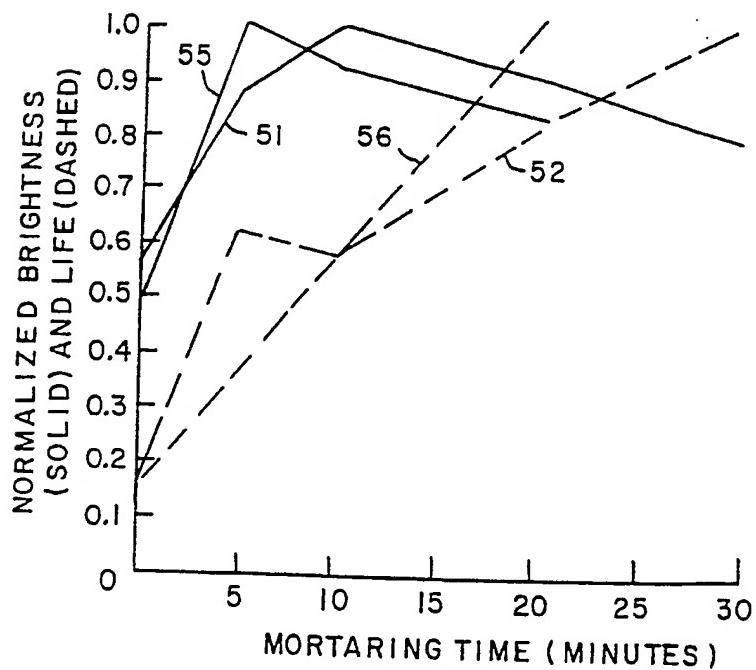


FIG. 4

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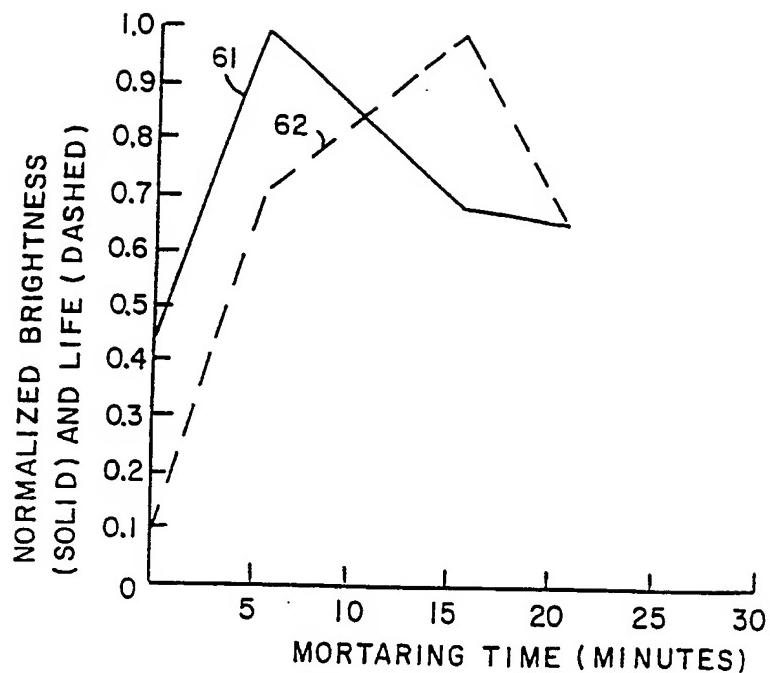


FIG. 5

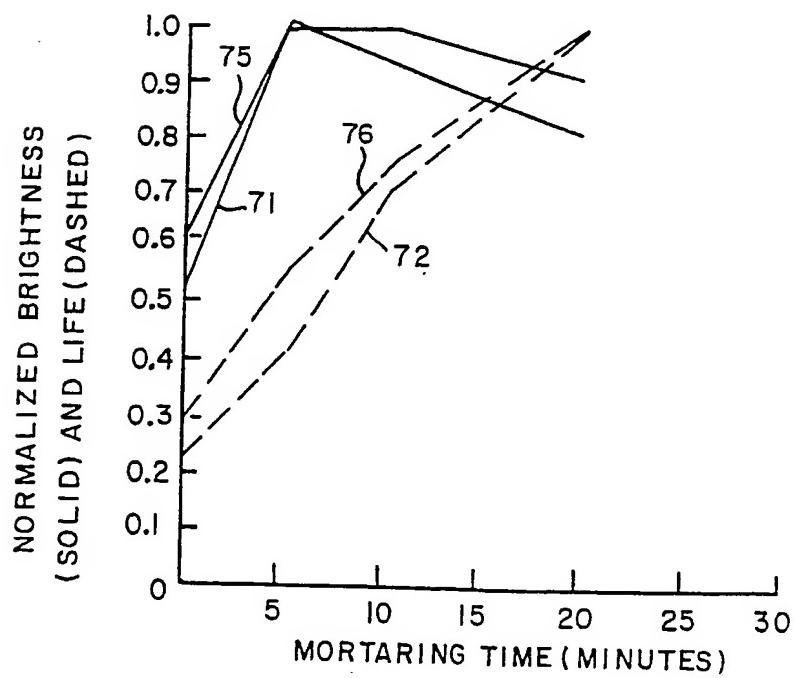


FIG. 6

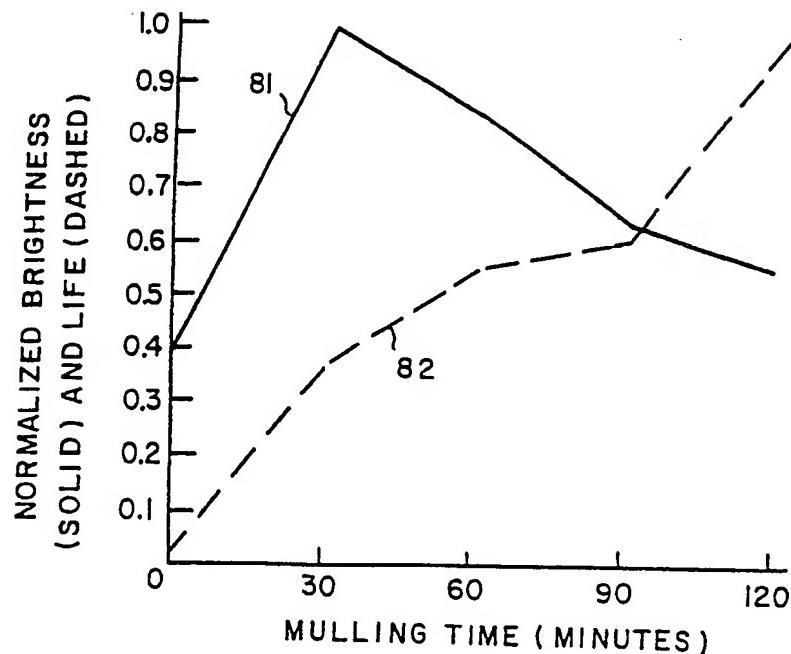


FIG. 7

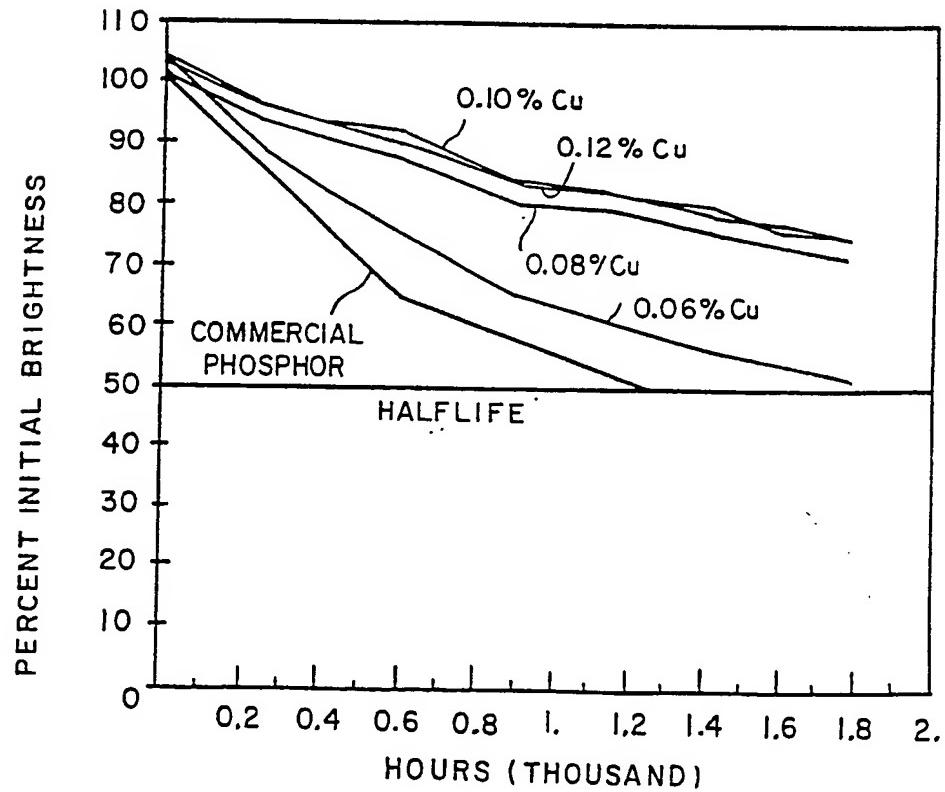


FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/02640

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) :		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5): H01J 1/62, 63/04 C09K 11/54		
US CL : 313/503,512,486 252/301.63		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System		Classification Symbols
US	CL	313/502,503,512,486 252/301.63
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched :		
III. DOCUMENTS CONSIDERED TO BE RELEVANT **		
Category *	Citation of Document, *** with indication, where appropriate, of the relevant passages ****	Relevant to Claim No. ***
Y	US, A, 4,859,361 (REILLY ET AL.) 22 AUGUST 1989 Col. 3, line 11, col. 2, line 2	1,2,3,4,5,6,14 15,16-21,22
Y	US, A, 4,104,555 (HEMING) 01 AUGUST 1978 Summary.	23
A	US, A, 2,957,830 (GOLDBERG) 25 OCTOBER 1960 Col. 1, line 42.	
Y	Hirabayashi and Kozawaguchi and Tsujiyama "AC Power Electroluminescence maintenance improvement" (JAPAN) See page 2449 & 2452 December 1983.	1,14,22
<p>* Special categories of cited documents: 13 "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search :	Date of Mailing of this International Search Report :	
06 JUNE 1991	19 AUG 1991	
International Searching Authority :	Signature of Authorized Officer: <i>Vietnam Nguyen</i> NGUYEN NGOC-HO	
ISA/US	BRIAN ZIMMERMAN INTERNATIONAL DIVISION	